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STUDY OF UNDERPOTENTIAL DEPOSITED COPPER ON GOLD BY
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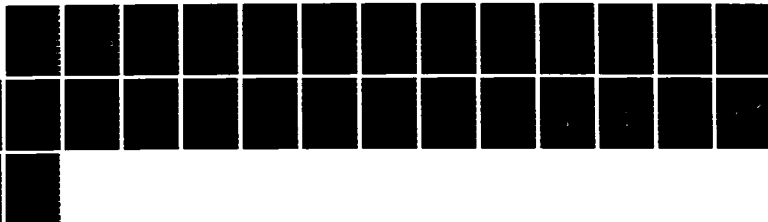
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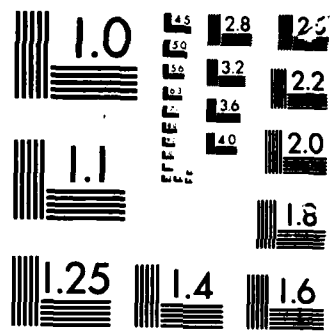
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #24	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Study of Underpotential Deposited Copper on Gold by Fluorescent Exafs		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) L. Blum, , H.D. Abruña, J. White, J.G. Gordon II, G. Borges, M. Samant and O.R. Melroy		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics University of Puerto Rico Box AT, Rfo Piedras, PR 00931		8. CONTRACT OR GRANT NUMBER(s) N00014-81-C-0776
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS TASK No NR 051-775
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE May 27, 1986
		13. NUMBER OF PAGES 23
		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) <div style="text-align: right;">DTIC ELECTE JUN 23 1986 S E D</div>		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of Chemical Physics		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Exafs, electrode, interface, structure		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) —Using grazing incidence geometry and fluorescence detection, surface EXAFS of a monolayer of underpotential deposited copper on epitaxially deposited gold (III) on mica was observed. The results are interpreted in terms of models in which the Cu-Oxygen distance is $1.07 \pm .03 \text{ \AA}$ and the Cu-Au distance is $2.55 \pm .06 \text{ \AA}$. The copper and three gold atoms at the metallic surface form an elongated tetrahedron, with the oxygen right on top of the copper. Two plausible models for the oxygen arrangement are proposed, one		

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OFFICE OF NAVAL RESEARCH
CONTRACT N00014-81-C-0776
TASK No. NR 051-775
TECHNICAL REPORT #24

STUDY OF UNDERPOTENTIAL DEPOSITED COPPER ON GOLD BY FLUORESCENT EXAFS

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PREPARED FOR PUBLICATION IN THE
JOURNAL OF CHEMICAL PHYSICS

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Using grazing incidence geometry and fluorescence detection, surface EXAFS of a monolayer of underpotential deposited copper on epitaxially deposited gold [111] on mica was observed. The results are interpreted in terms of models in which the Cu-Oxygen distance is 2.07 ± 0.03 Å and the Cu-Au distance is 2.55 ± 0.06 Å. The copper and three gold atoms at the metallic surface form an elongated tetrahedron, with the oxygen on top of the copper. Two plausible models for the oxygen arrangement are proposed, one with only one oxygen right on top, and another one with a sulfate ion. This second model yields a slightly better fit of the data.

Our knowledge of the structure of the polarized interface between a conducting electrode and a ionic solution has been, up to recent times based on indirect evidence provided by measurements of capacitance, surface excess concentration, surface tension, or other macroscopic electrical or thermodynamic measurements, which depend mostly on averages over large portions of the interface. The electro-optical measurements are also of the same nature, since the wavelength of the light is of the order of 1000 \AA . These measurements can be interpreted in terms of simple and reasonable models which may be our best microscopic picture of the interface. The problem is that there are many models that will fit the data of a given electro-thermodynamic experiment. There is no substitute for a direct structure determination. But because of the fact that the surface to volume ratio is so small, these experiments have to be carried out in ultra high vacuum. The information obtained from these experiments show, that indeed, the adsorbate on a metallic surface is very complex [1], and that it can undergo a rich variety of phase transitions. For example, it can be ordered and commensurate with the metal lattice, or it can be incommensurate and still ordered, and finally, it can also be amorphous or mobile on the surface.

Ex-situ experiments on interfaces of interest to electrochemists have provided a wealth of very interesting and revealing information. The work of Yaeger [2], Hubbard [3], Ross [4], Sass [5] have shown that in many cases, the adsorbed layers on Cu, Pt, Ag, Au and other metals of electrochemical interest form mostly ordered phases commensurate with the metallic underlayer.

It is an open question to see whether the removal of the interface from the electrolytic cell does not change the structure. Indeed, in the case of a polarized electrode the fields can be large. Furthermore, much of the interesting properties of the electrodes are due to the solvent effects, and indeed the theory predicts that the thermodynamic and kinetic properties should depend strongly on the nature of the solvent.

It is therefore important to have techniques that can probe the surface in situ. Such are the techniques of optical spectroscopy. The work on the surface enhanced Raman effect (Fleischmann [6], Van Duyne [7], Surface infrared spectroscopy (Pons [8], Bewick [9]), surface plasmons (Gordon [10]) and second harmonic generation (Shen [11], Philpott [12]) have thrown light on important questions regarding the structure and state of adsorbates at the charged interface. However, these spectroscopic measurements probe the bond polarizability and does not yield structural information directly. In actual fact, if the structure were known, then one could infer from these experiments local fields and field gradients, which are extremely interesting quantities.

Among the surface sensitive structure determination techniques, fluorescence surface EXAFS (FSEXAFS) seems to be the one that has the unique characteristics needed to provide information about the environment of an adsorbed ion at the electrode interface [13,14]. It is based on the modulation of the x-ray fluorescence produced by the backscattering of a photoelectron by atoms neighboring a given central atom. The point is that this photoelectron can be selectively emitted by a beam of x-rays in resonance with the energy of the lowest level of the atom (usually the K or L lines). Since it is essentially an electron scattering process, it has the same drawbacks as this technique, in the

sense that the interpretation of the results is not only dependent on the scattering cross sections of the individual atoms, but also on the chemical environment and bonding. On the other hand it does 'see' all the neighbours, even light elements such as oxygen can be detected without major difficulties. This is different from the x-ray diffraction technique, in which the cross section is a function of the square of the atomic number and therefore, heavy elements will tend to obscure the signal from the lighter ones. Another advantage of the technique is that the analysis of the near edge structure (XANES [15]) yields information about the state of oxidation of the central atom.

Using a transmission technique, Kordesch and Hoffmann [16a] monitored the EXAFS spectrum from passivated iron films in an electrolyte. To obtain a good signal to noise these authors used multiple layers of the films. A similar experiment for passivated nickel films was recently reported by Bosio, Cortes and Froment [16b], who used a reflection geometry. In our first series of experiments (Gordon [17]), we tried to obtain the FSEXAFS signal from Br and Pb on silver [11]. Even with very thin electrode films the signal to noise ratio was too poor to give any meaningful interpretation. To obtain spectra of sufficiently good quality we found it necessary to use the grazing angle technique of Heald and Stern [18], in which the x-rays are almost parallel to the surface of the metal. This produces an enhancement in the intensity, and also, because now the penetration depth is small, a decrease in the background scattering. This technique was used recently by Lairson et al. [19] to study bromine adsorbed on a nickel [001] surface.

In our first series of experiments (Gordon [20]) we looked at electrochemically deposited iodine on platinum. The absorption edge of

the x-rays was very well defined in this case, but the signal was too small and damped out. Still, by a noise filtering technique we were able to obtain a distance for the Pt-I bond of 2.63 Å, which is somewhat shorter than what one would expect, but not unreasonable in view of the weakness of the signal.

In the present communication we report observations of underpotential deposited [UPD] copper on gold [111] surfaces. These experiments were also performed at the CHESS synchrotron of Cornell University using the grazing angle technique and under potentiostatic control. This time a well resolved EXAFS pattern was obtained from a monolayer deposit of copper. The analysis of the spectra using the theoretical phase shifts and amplitudes of Teo and Lee [21] and also the features of the near edge spectra, shows that it is not possible to interpret it in terms of backscattering from the Au atoms alone. If we include also the backscattering of a light element such as oxygen, then we can fit the experimental data with a geometrical model of the surface in which the copper is at the center of an elongated tetrahedron, in which one of the corners is occupied by the oxygen and the three others, which form part of the gold surface.

EXPERIMENTAL

The experiments were carried out at the C-2 beam line of the CHESS synchrotron of Cornell University. The sample was an epitaxially grown film of gold on mica. This film is a textured polycrystal with a [111] surface, of about 35x100 mm in size. It was mounted at the end of an lexan holder, suspended inside a rectangular lexan cell with mylar

windows which can be filled with electrolyte. The holder is attached to a rotating stage which permits a full 360° rotation with about 2° setting accuracy, and a finer control which has a $.02^\circ$ accuracy over a 5° range. The detector was a high purity germanium solid state detector (EG&G ORTEC) with a maximum energy resolution of about 360 eV, but in the actual conditions of our experiment was 600 eV which is enough to discriminate the fluorescent signal from the Compton and elastic background contributions. It was fitted with nickel filters and Soller slits to further isolate the K-edge of the Cu fluorescence, which occurs at 8.03 KeV., from the elastic and Compton scattering. The gold sample was prepared at the IBM research facility in San Jose, CA. The copper was deposited from a 2×10^{-5} M solution of CuSO_4 in 1M H_2SO_4 . During the electrodeposition of the copper the level of electrolyte was raised to cover entirely the active area of the electrode. After deposition the level was lowered. The electrode was covered, at all times, by a $.005''$ inch thick mylar film, which held the electrolyte by capillary action. The deposition potential was .13 V against a 3M KCl/Ag/AgCl reference electrode. The potential control was checked by the measurement of the Cu absorption edge after stripping the UPD copper monolayer, which was 4 eV, as it should. This was done for every set of runs. The data was collected using the CHSS XOPLUS program, and the initial analysis was performed using Brian Kincaid's EXAFS program.

RESULTS AND THEIR INTERPRETATION

In all of our experimental runs the gold surface was kept vertical, so that, since the polarization of the synchrotron beam is horizontal, it will be parallel to the bonds that are perpendicular to the surface and,

viceversa, perpendicular to the parallel ones, which, as we will see it, will not contribute to the FSEXAFS in this geometry.

For the excitation of a s level electron (the K edge) [22], the absorption coefficient χ (which is related to the fluorescence intensity by a logarithmic relation) is given by

$$\chi(k) = (\mu - \mu_0) / \mu_0$$

$$= \sum_j 3 \cos^2 \theta_j N_j F_j(k) e^{-2\sigma_j^2 k^2 - 2r_j / \lambda_j} e^{i \sin[kr_j + \phi_{ab}(k)] / kr_j^2} \quad (1)$$

where $F_j(k)$ is the backscattering amplitude from each of the N_j neighboring atoms of type j , with a Debye-Waller factor σ_j^2 (to account for the thermal motion of the atom), and r_j which is the distance to the central atom. θ_j is the angle between the polarization vector of the x-rays and the direction of the bond to the j atom. The parameter λ_j takes into account the inelastic scattering losses of the photoelectron. To a reasonable approximation the phase shift of the backscattered electron is given by

$$\phi_{ab}(k) = \phi_a(k) + \phi_b(k) - \pi \quad (2)$$

where $\phi_a(k)$ is the phase shift due to the central atom, and $\phi_b(k)$ is that of the backscattering atom. When the backscatterer is a heavy element, there is a strong resonance at about $k = 6 \text{ \AA}^{-1}$, which corresponds to an absorption peak for the electron (and a dip in the scattering amplitude $F_j(k)$). This feature is illustrated in fig. 1, where we display results of Teo and Lee [21]. The general observation is that the phase

shift factors are not very sensitive to chemical environment [22], which is unlike the amplitude factors. In figure 1 we have plotted also the corresponding Pt curves, which are close to the ones of Au. These strong features are a mixed blessing, since they preclude the direct use of Fourier transforms in the interpretation of the spectra. But on the other hand, they will produce a very characteristic signature at $k=6 \text{ \AA}^{-1}$ in the spectra. Our present analysis of the experimental data is based on this feature.

The spectra obtained by signal averaging is shown in fig. 2. For comparison, we show also the raw spectra of CuSO_4 (fig. 3), and that of a Cu-Au alloy. In the solution pattern we notice a very sharp near edge peak (previously observed in similar Cu^{+2} solutions [23]), while the EXAFS spectra is strongly damped, which is an indication of large Debye Weller factors, or loosely bound hydration shell. For the Cu in the alloy the near edge structure is very different, since it shows a small double peak, and then a number of well defined oscillations in the far from the edge structure.

The absorption edge of the x-rays in our spectra is shifted by 4 eV to higher energies, which is consistent with the increase in the oxidation state of Cu. This observation was used in the stripping of the Cu monolayer after the runs.

The background was removed by fitting a second degree polynomial to a preselected portion of the spectra. The base line was insensitive to the size of this region, as long as it was of a reasonable size (>500 eV). When the background is removed and the scale is blown up, we get a pattern that is shown in figs. 5, 6 and 7. In our analysis we have picked the region between 4 and 13 \AA^{-1} . If we assume that the backscattering is

due only to gold, then the best fit is obtained for the unreasonable distance of 3 Å. But more importantly, the feature due to the resonance is missing altogether from our spectra. This is shown in fig. 5, with an unrenormalized intensity. If the only backscatterer is oxygen, then the fit is much better, as is shown in figure 6. A distance of 2.1-2.12 Å is obtained. Clearly, this model is saying that the Cu is surrounded by water only, which is inconsistent with the near edge structure, which corresponds to Cu metal more closely. And indeed the pattern has a series of well defined oscillations, which is different from the case of the solution. The answer to this puzzle is obtained by assuming that what we see is the copper in reduced form bound to the gold atoms of the surface, and with a strongly bound oxygen atoms right on top of it. The fit to this kind of model is shown in figure 7. There are a number of models that are consistent with the data: In figure 8a we have drawn a model that assumes only one oxygen on top of the copper presumably from an OH group. The best fit of the data to this model yields a distance of 2.05 Å for the Cu-O bond and 2.5 Å for the Cu-Au bond. The error in the assignment of the latter distance is necessarily much bigger than for the distance to the oxygen. A second plausible model has a sulfate ion sitting on top of the copper as shown in figure 8b. Since in this case the weight of the oxygen backscattering is about four times that of the former model, the oxygen part clearly dominates. In this case the best fit corresponds to a distance of 2.08 Å, for the same Cu-Au arrangement. It is clear that because of the noise in the spectra beyond $k=10 \text{ Å}^{-1}$ the error in this last distance is larger. This model yields a lower value of the mean square deviation, and also is consistent with the fact that in solution the sulfate ion tends to associate to

copper.

The distance of 2.5 Å for the Cu-Au bond is not too different from the one reported by Palmberg and Rodin [24] for the distance between copper and gold on an [001] surface. ^(2.56 Å) The Cu-O distance is well within the accepted values for crystalline compounds (which however are Cu⁺⁺) [25] and very close to that reported for solutions [26].

We must insist however, that these may not be the only models consistent with the data.

Acknowledgements: We are indebted to Dr. J. Smith for his interest and support, to Prof. H. L. Friedman for discussions and to Prof. C. Barnes for the PLUTO crystallographic plots.

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FIGURE CAPTIONS

Figure 1: Phase shifts and amplitudes for Au and Pt. Data taken from ref [21]. Units for k are inverse Angstroms. The values for Pt, shown as an illustration that the resonance is not strongly dependent on chemical environment, are the dots.

Figure 2: Raw spectra of UPD Cu monolayer on Au [111]

Figure 3: Raw spectra of CuSO_4

Figure 4: Raw spectra of 2% Cu-Au alloy.

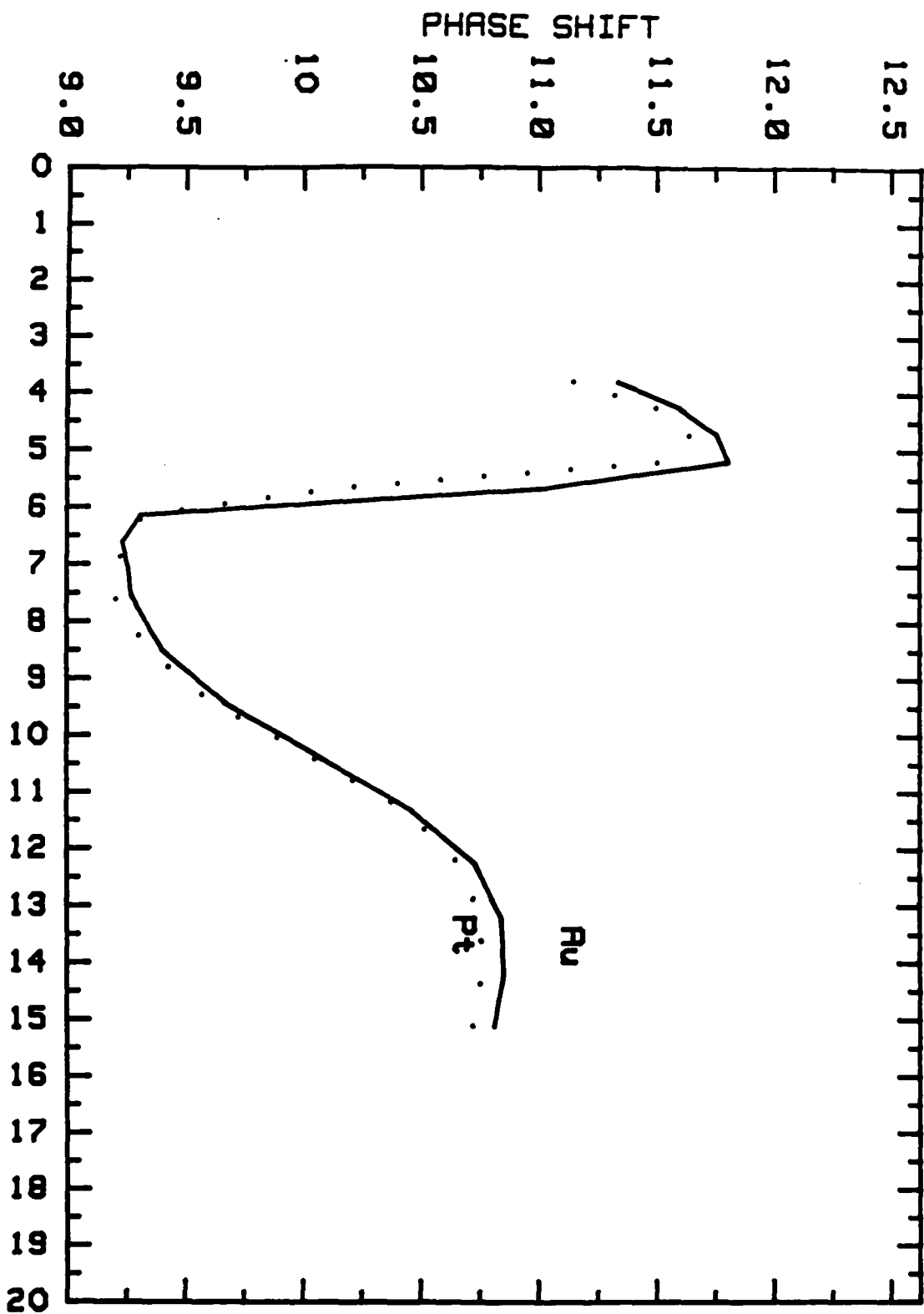
Figure 5: Data after background removal (+). The curve is the theoretical fluorescence from eq.(1) using only Au backscattering. The distance is 3 Å. Units for k are inverse Angstroms.

Figure 6: Same as fig.5, but fitted to oxygen as the sole backscatterer.

Figure 7: Same as fig.5 fitted to the model of fig.8b.

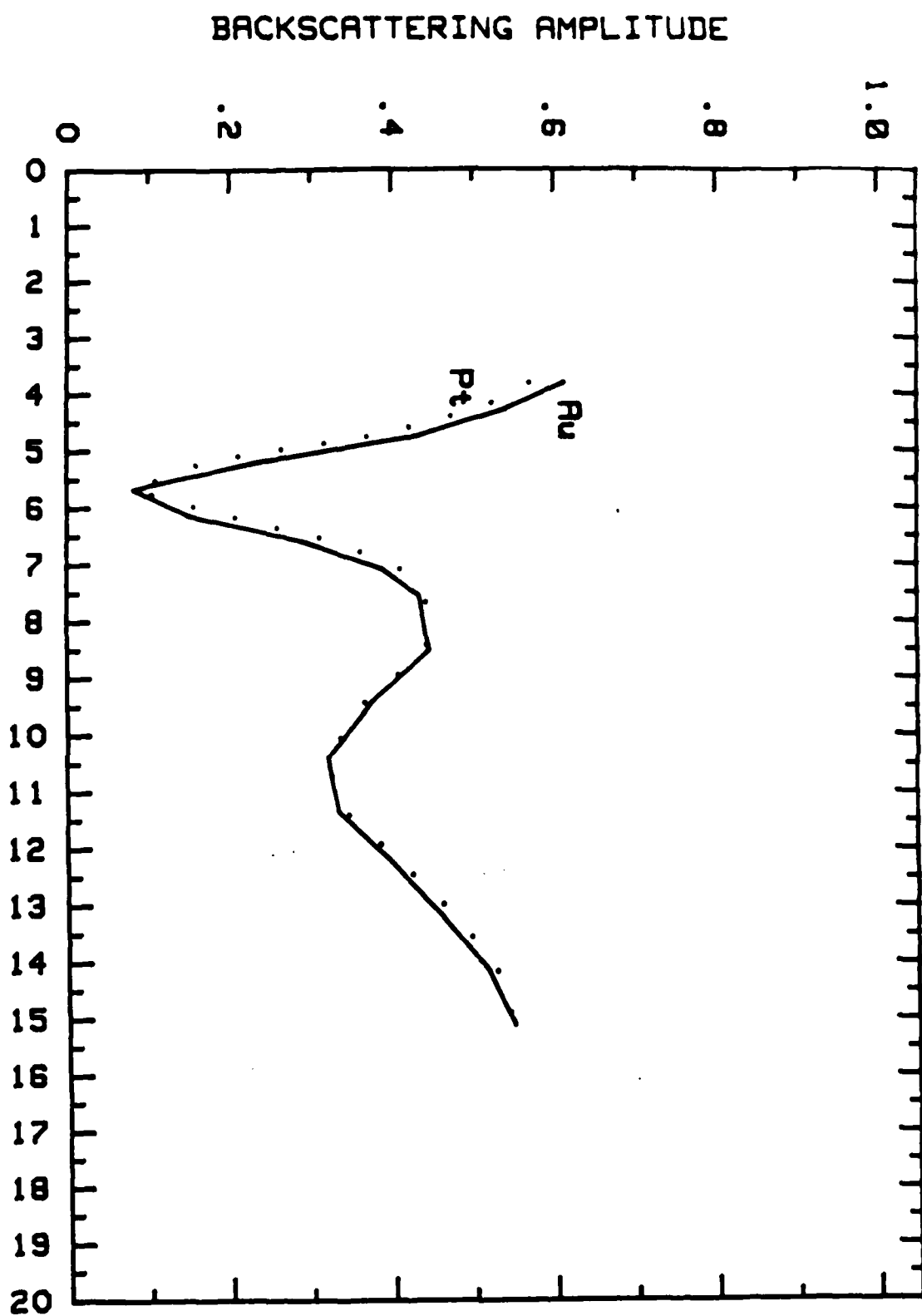
Figure 8a: Plausible geometrical arrangement of the Cu and O atoms on the Gold [111] surface.

Figure 8b: Plausible geometrical arrangement of the Cu and SO_4^- on the Gold [111] surface.



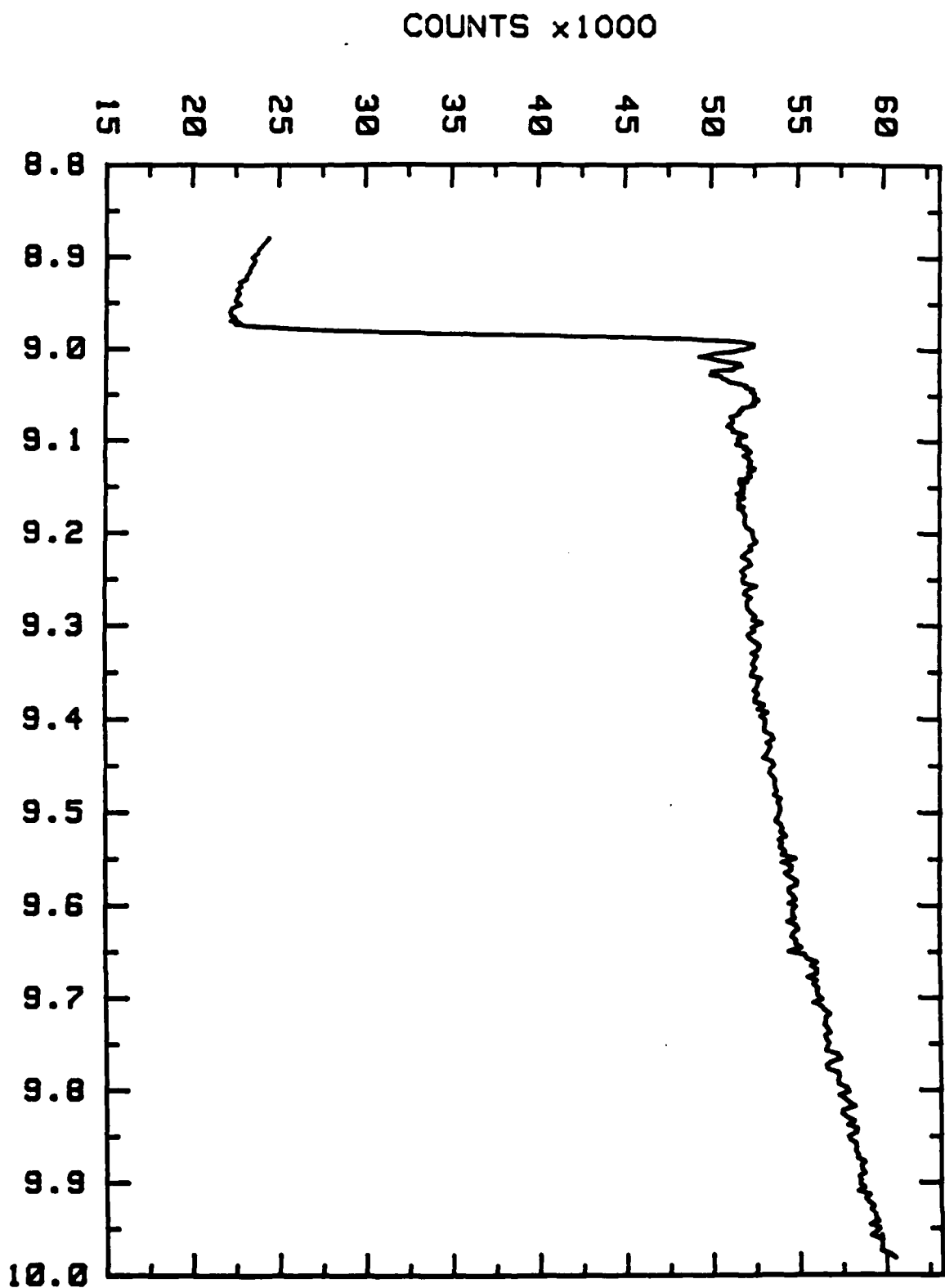
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FIGURE 1a



K

FIGURE 1b



key

FIGURE 2

INTENSITY

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-13

-13.5

-14

9000

9250

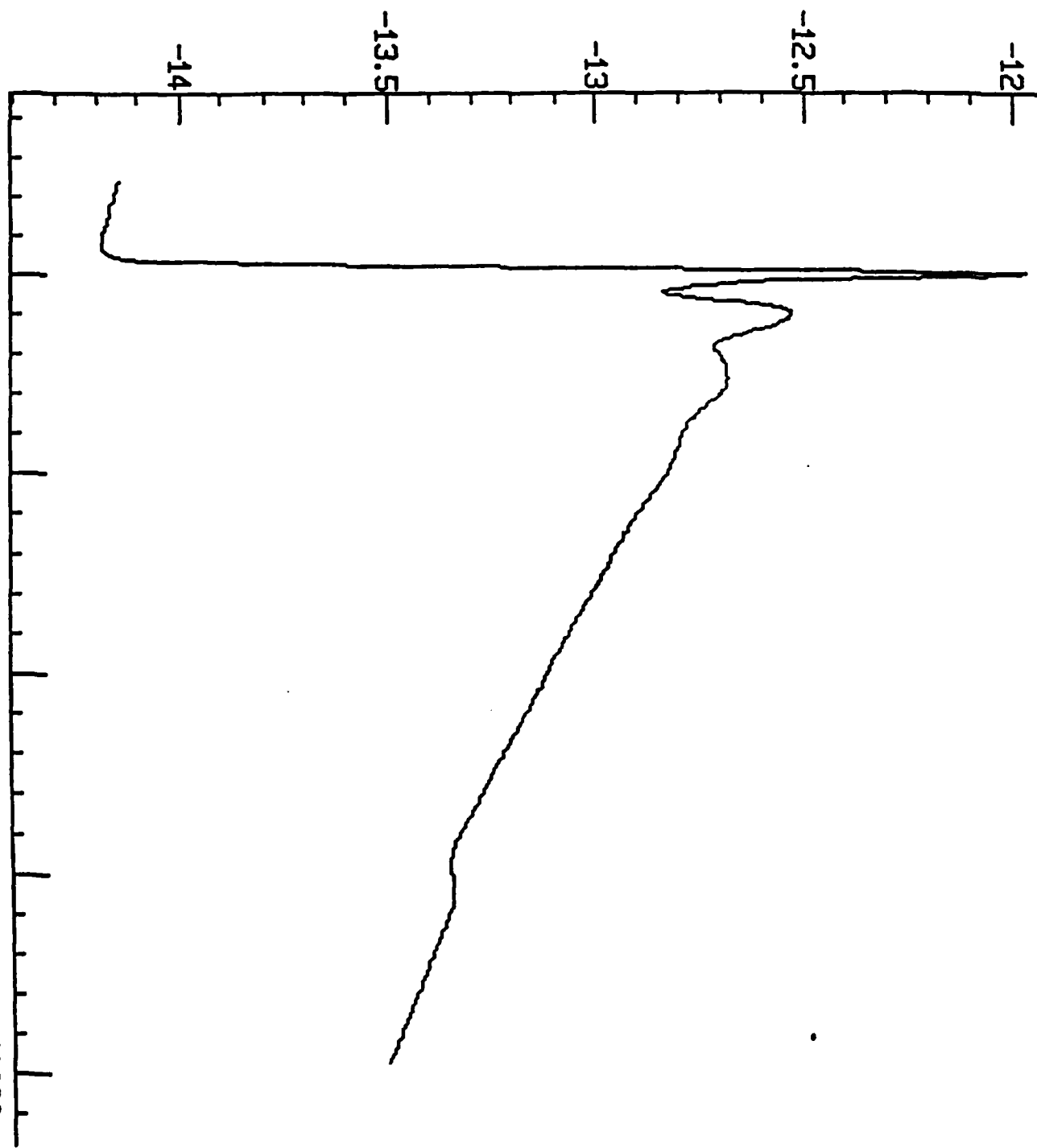
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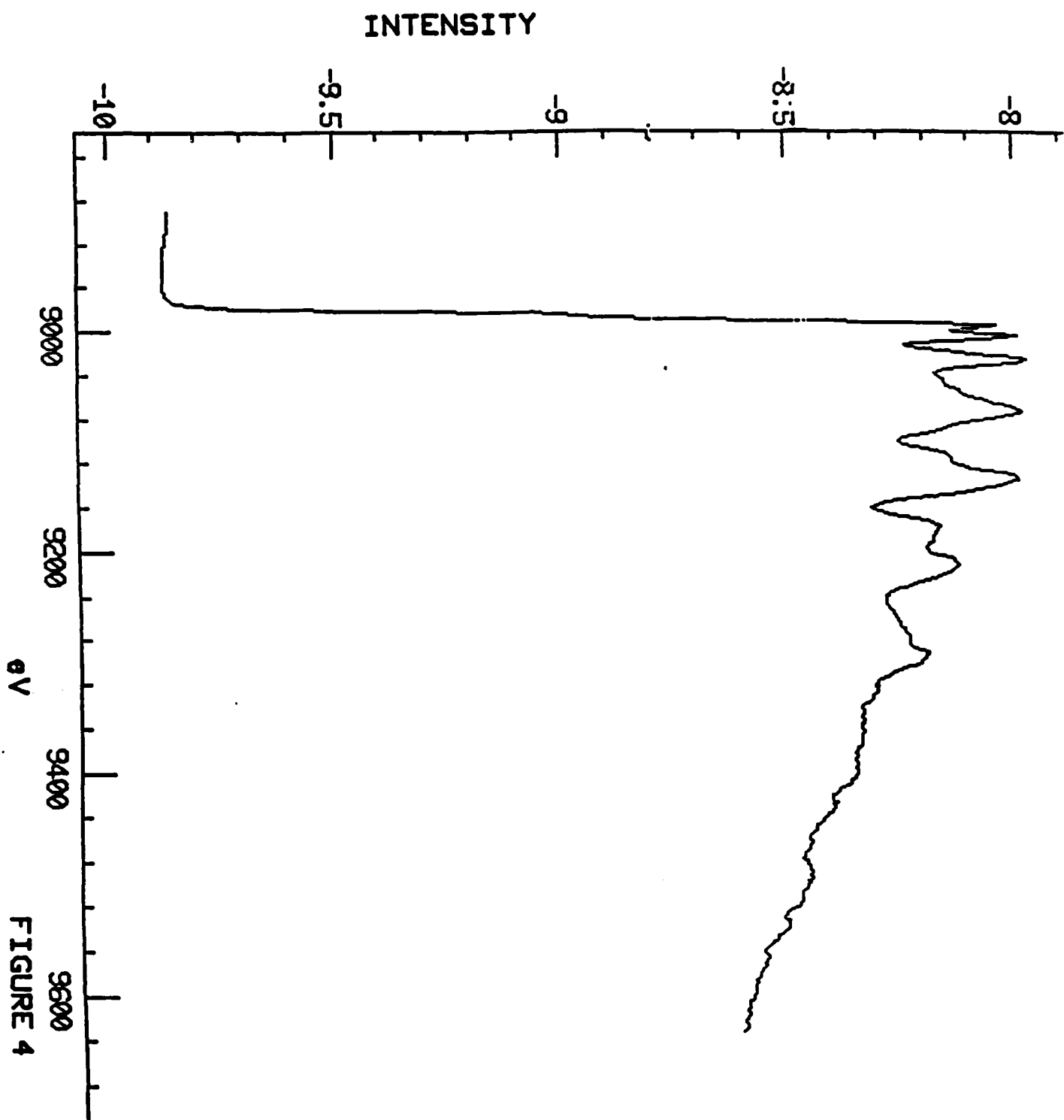
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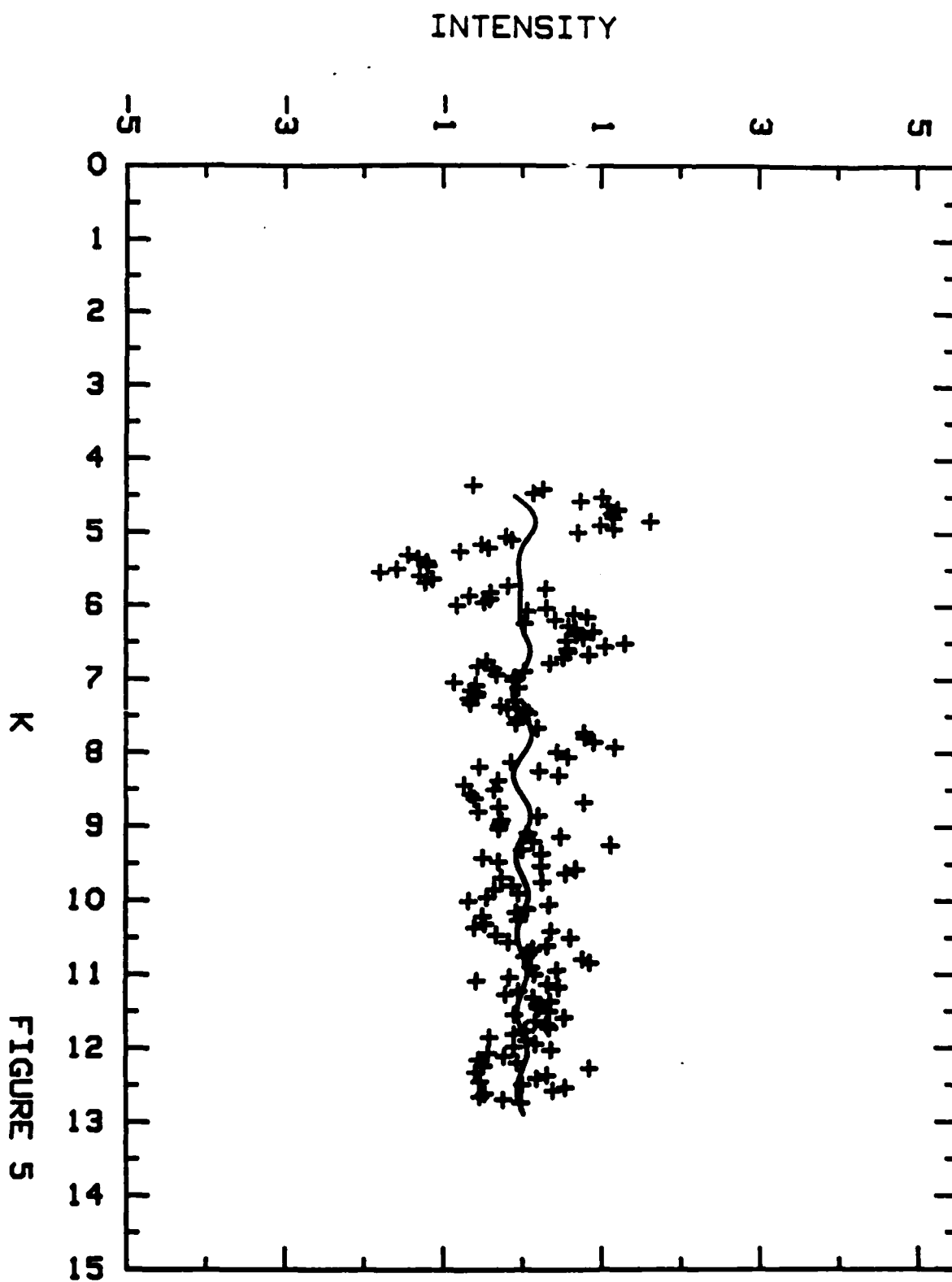


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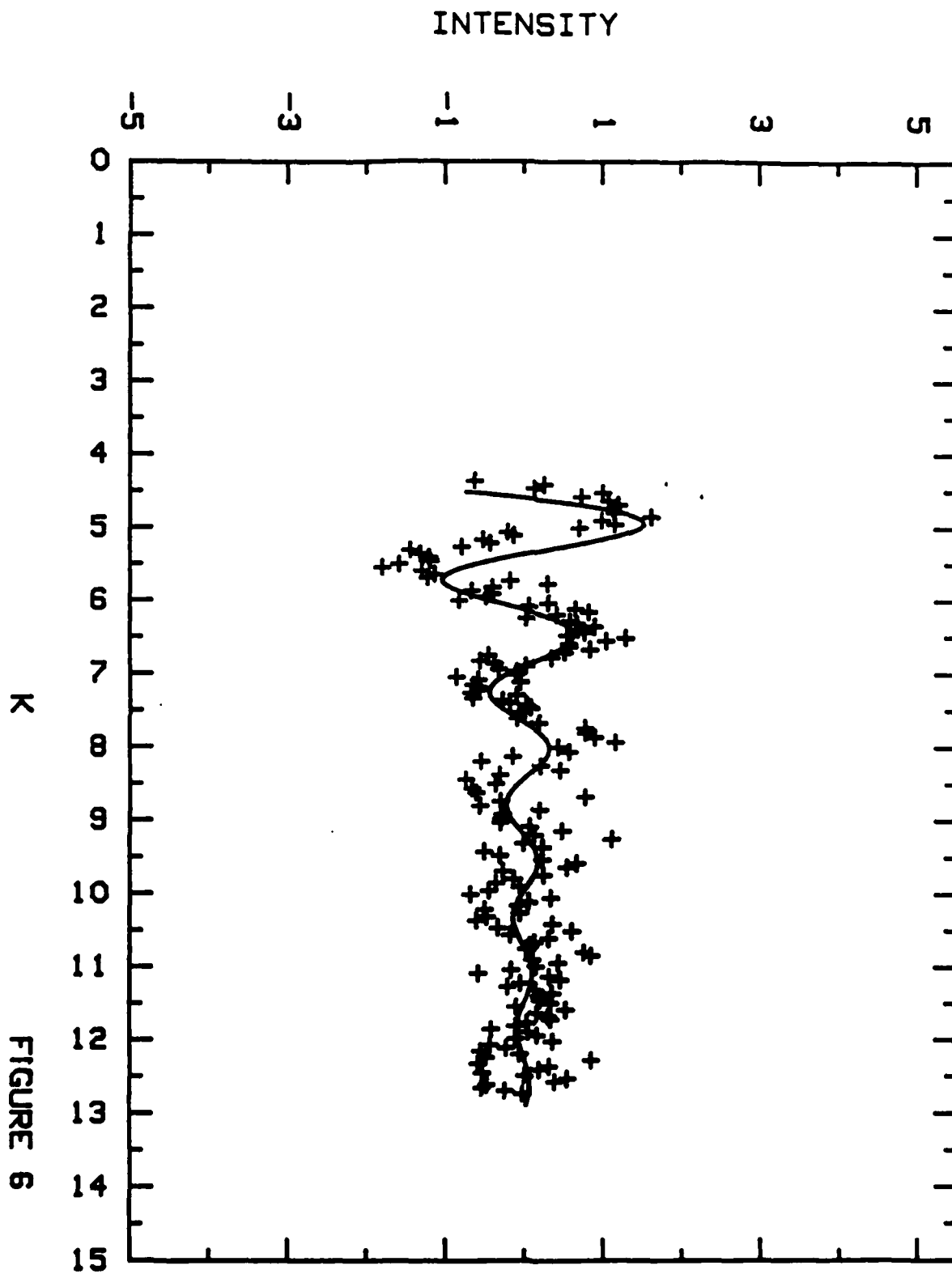


FIGURE 6

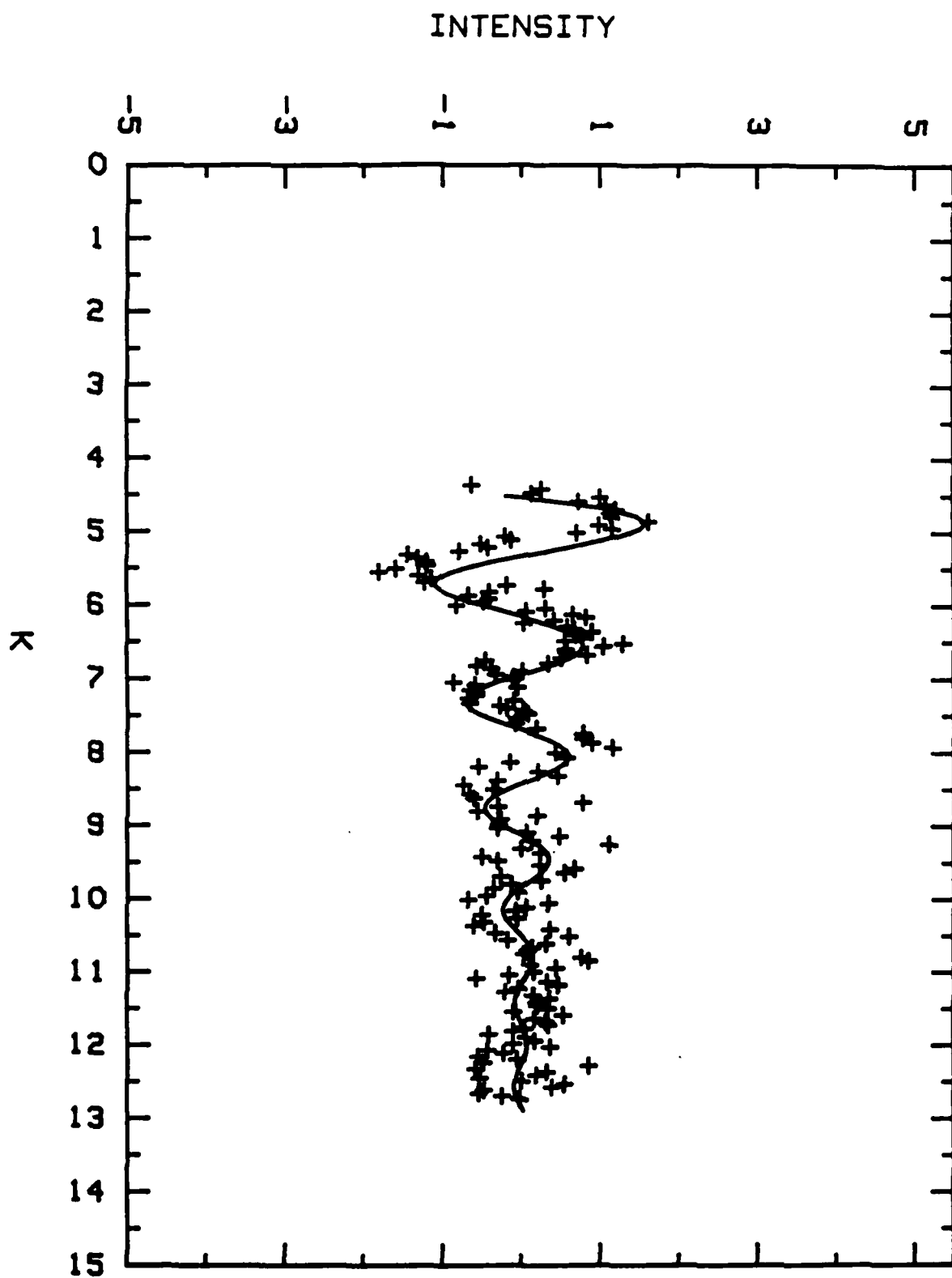
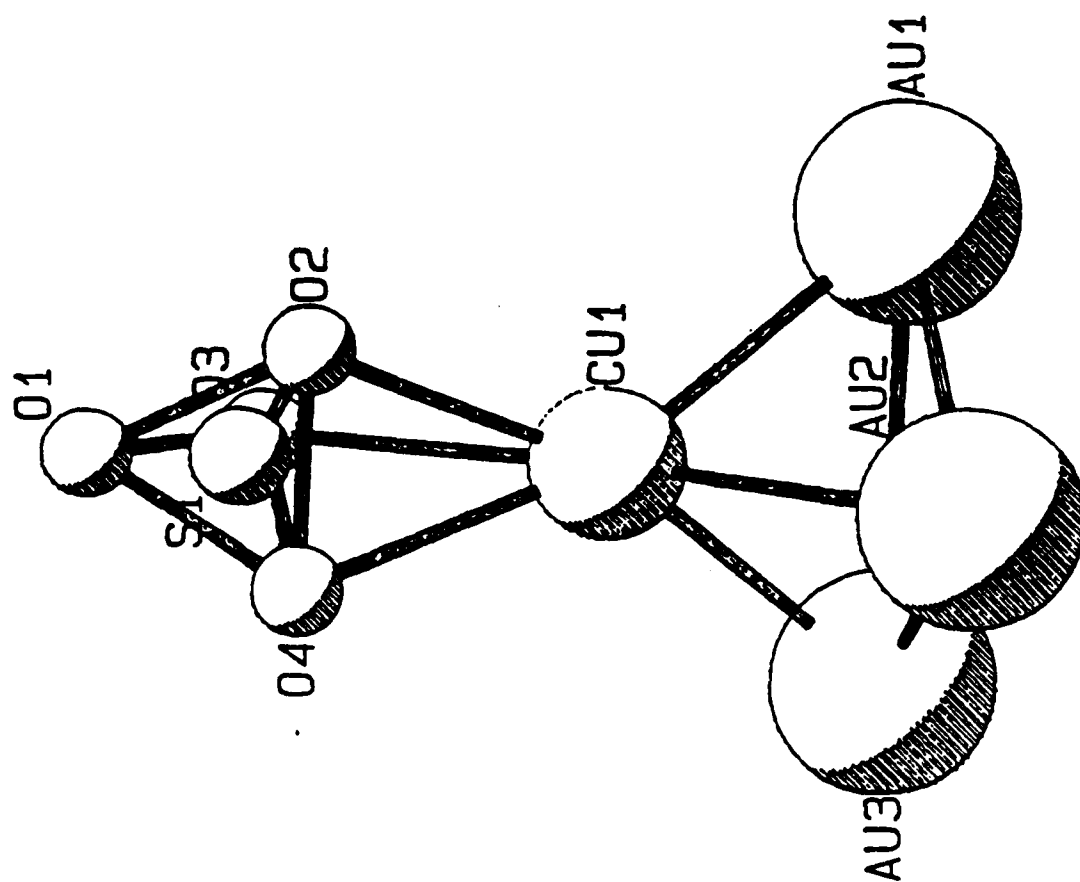


FIGURE 7



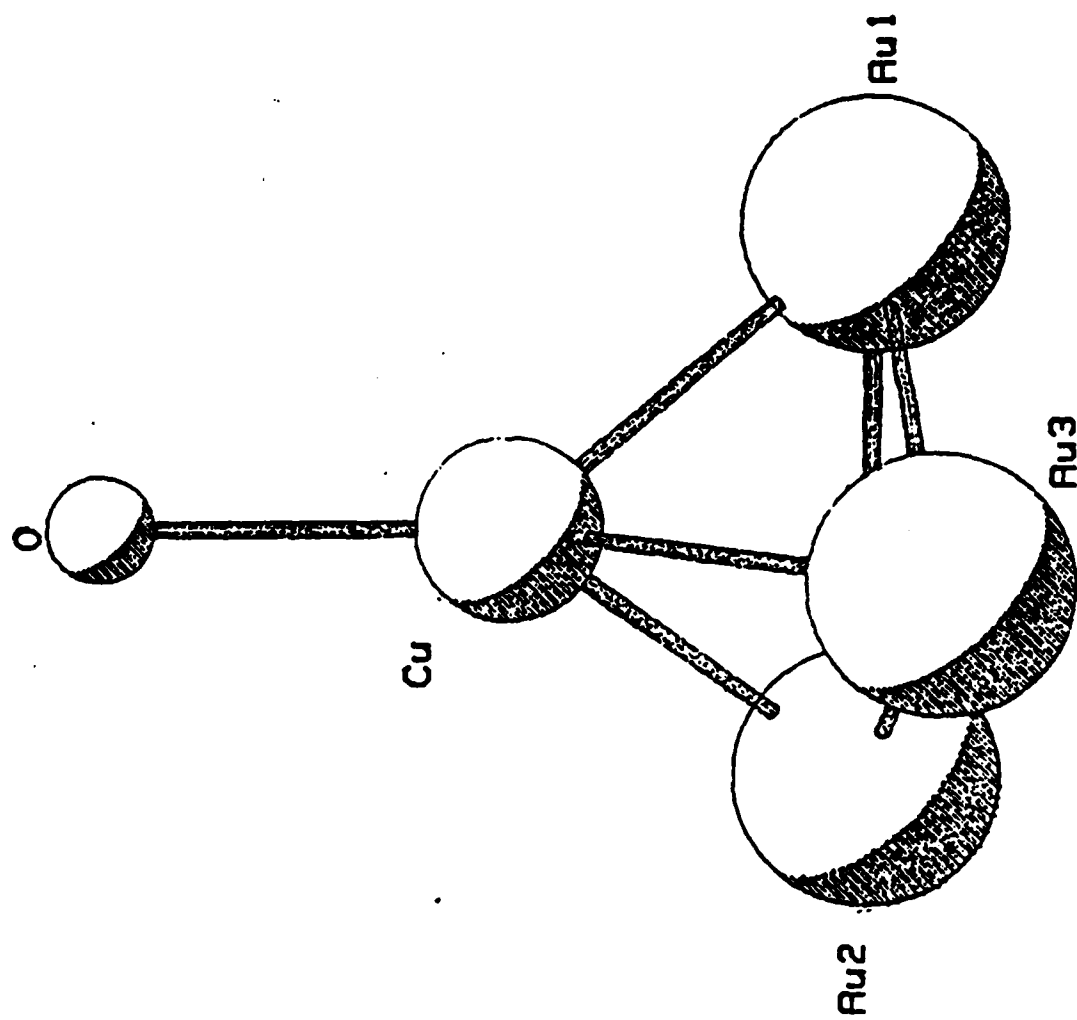


FIGURE 8a

UPD COPPER ON GOLD

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